Materials Degradation Processes In Elevated-Temperature Environments Related To Process Heating

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UT-BATTELLE

Process Heating Applications Often Involve Aggressive Environmental Conditions

- High temperatures

- Reactive species
  - Nitriding
 - Carburizing
  - "Oxidizing"
  - Combustion gases

- Salts

Materials degradation by high-temperature corrosion & environmental effects comprises a key limiting set of phenomena in process heating

This Is Manifested In Important Materials Needs

- Longer-lived heating devices (elements, radiant tubes)

- Improved refractories and insulation

- Better materials for recuperators, other heat exchangers, and fans

- Weight reduction for furnace hardware by improved corrosion resistance

- Protection of sensors

There are active research projects in most of these areas in support of materials for energy production and utilization and industrial applications

Substantial Effort Devoted To Creep- And Oxidation-Resistant Alloy Foils For Thin-Wall Applications
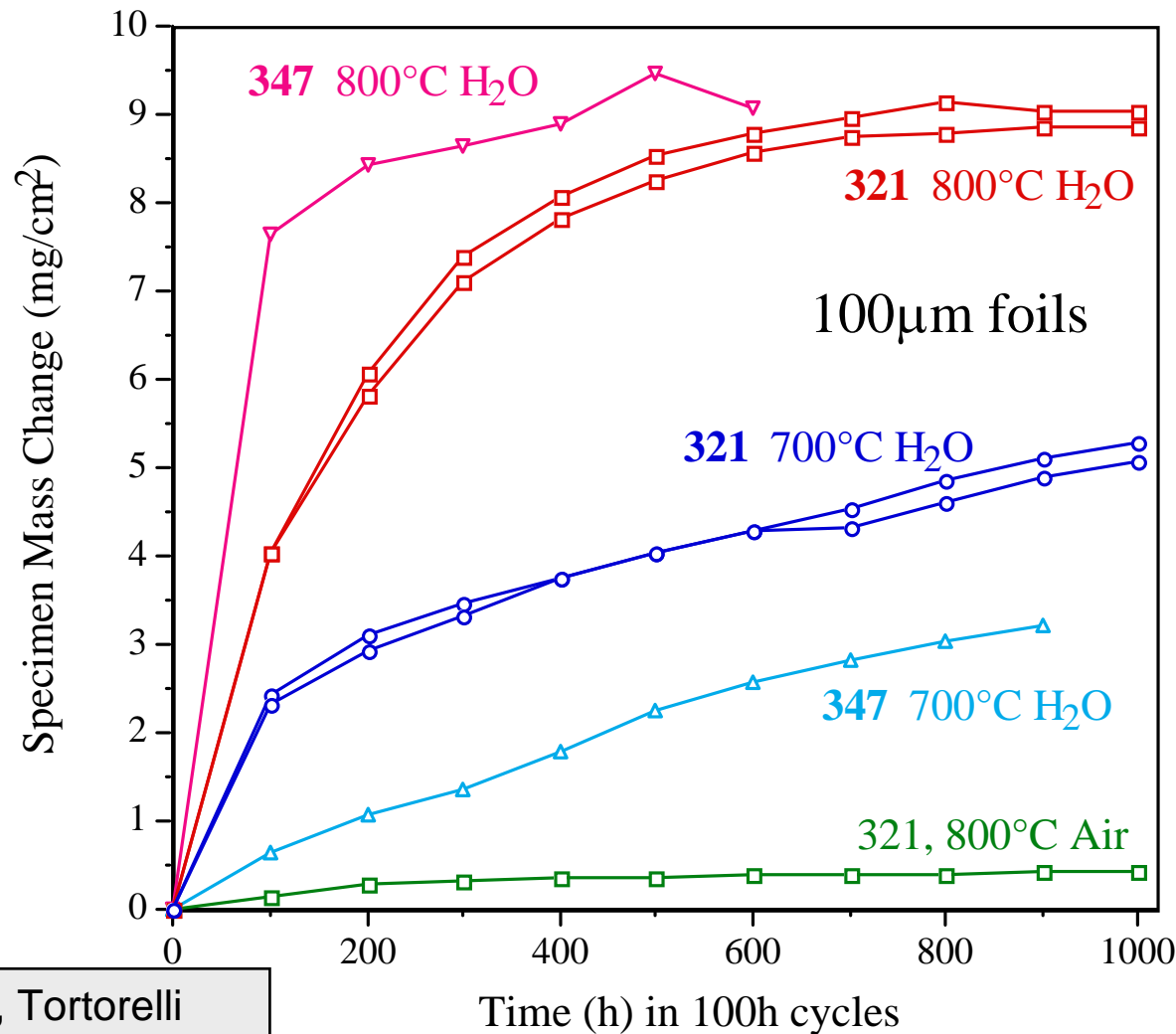

Capstone

10 mm
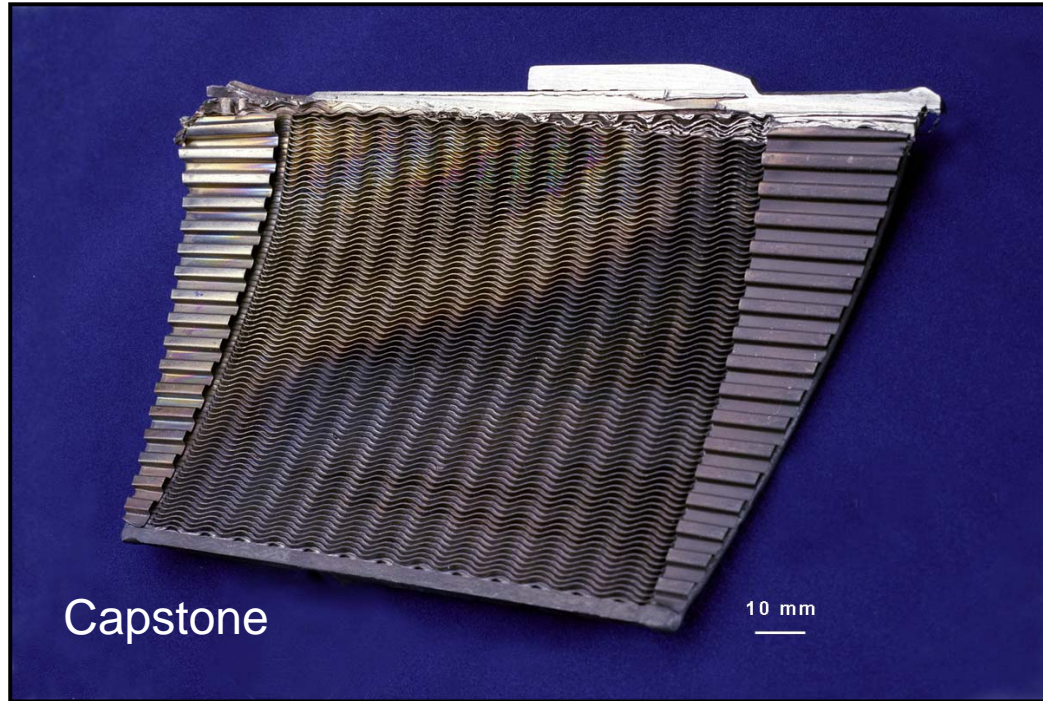
Primary Surface
Recuperator (PSR)

Recuperators for high-efficiency microturbines

- Higher temperatures require improvements in strength and oxidation resistance

- Significant progress has been made in both areas

Maziasz, Pint, Swindeman,
More, Lara-Curzio

Water Vapor (Present In Combustion Gases) Can Significantly Degrade Oxidation Resistance

347 800°C H_2O

321 800°C H_2O

100μm foils

321 700°C H_2O

347 700°C H_2O

321, 800°C Air

10% H_2O

Specimen Mass Change (mg/cm²)

Time (h) in 100h cycles

Pint, More, Tortorelli

Various commercial alloys, and variants thereof, being evaluated for better high-temperature creep and oxidation behavior

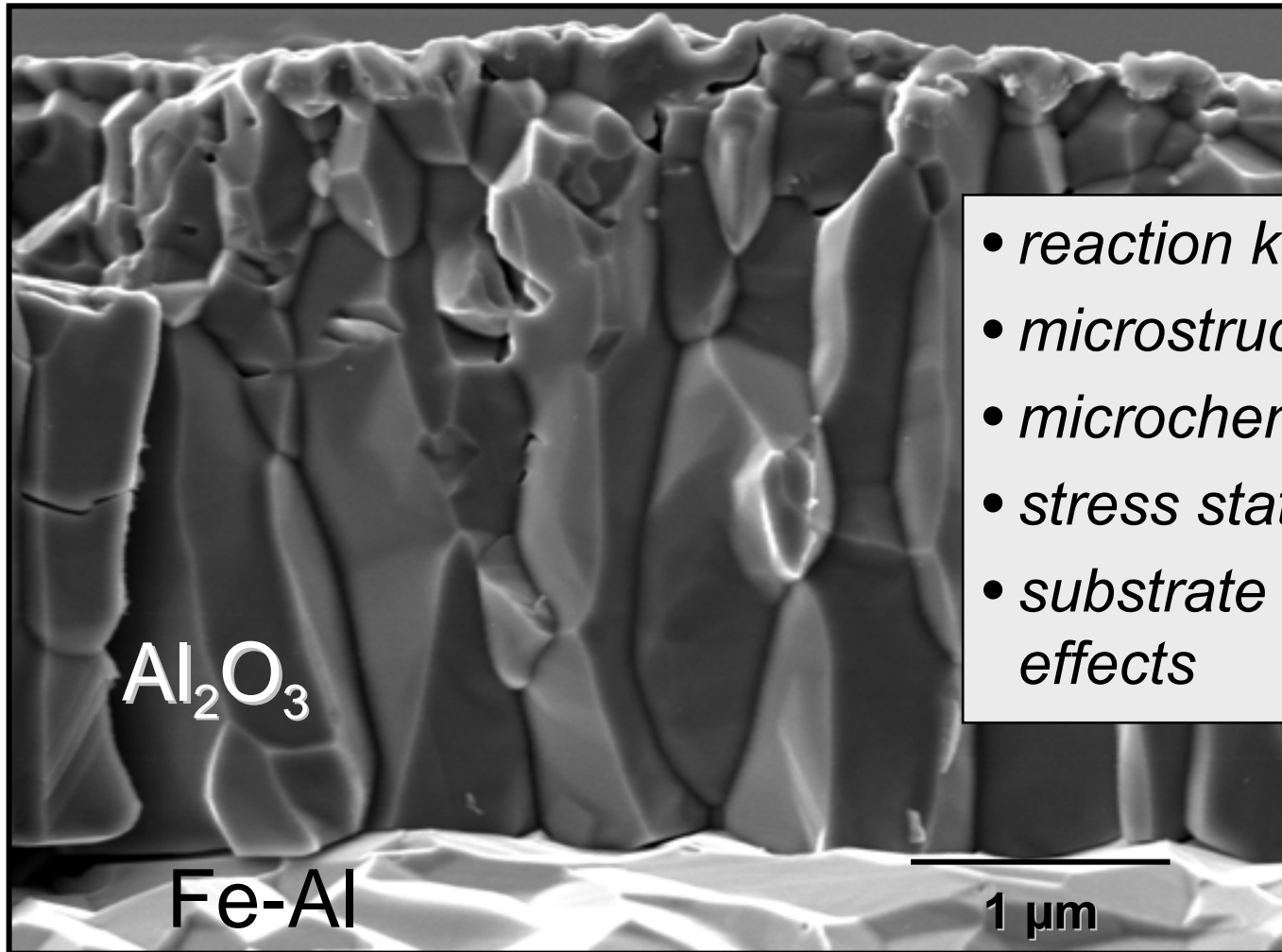# Work On Model Alloys Has Led To Alloy Compositon Maps For Resistance To Water Vapor Effects

Fe-Cr(-Ni)
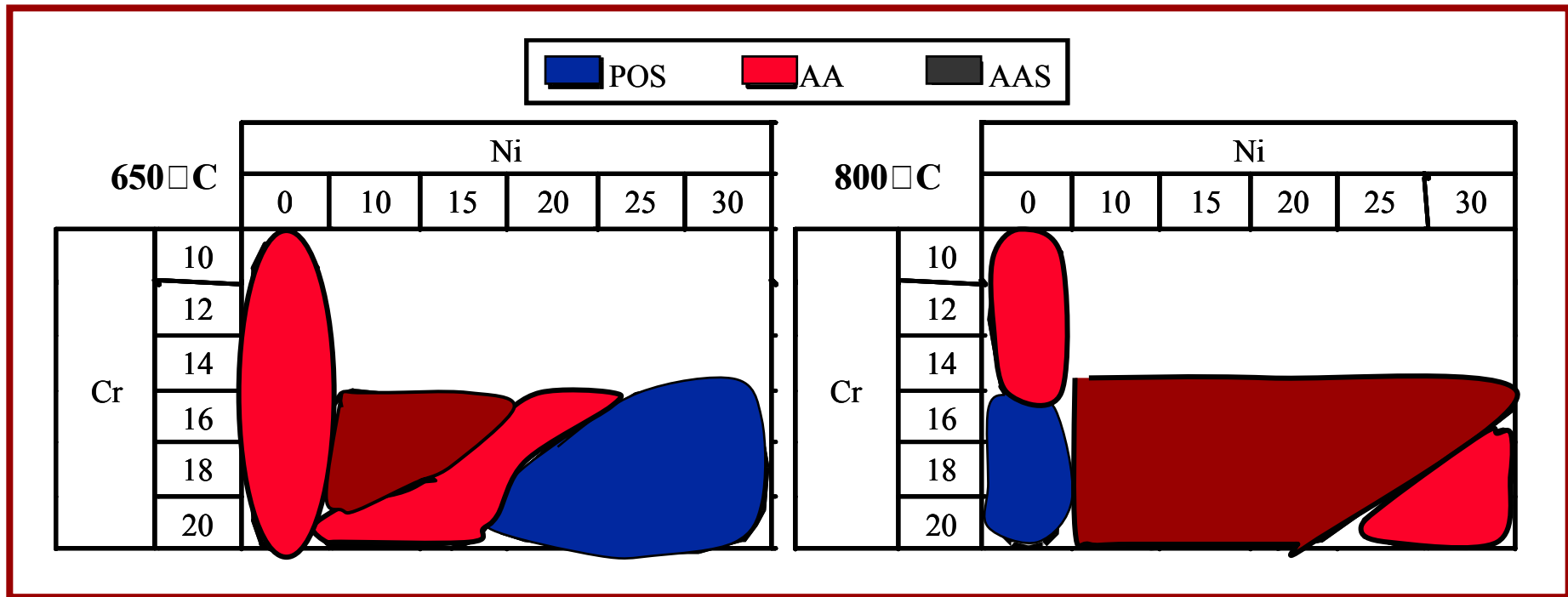
AA: accelerated attack (relative to dry air)
AAS: accelerated attack with spallation
POS: protective oxide scale development

Peraldi & Pint

Much Of Oxidation Work Focuses On The Ability To Form <u>Protective</u> Product Scales

- *reaction kinetics*
- *microstructure*
- *microchemistry*
- *stress states*
- *substrate comp'n. effects*

Al_2O_3

Fe-Al

1 µm

*Example: Ni$_3$Al for furnace hardware*

High-Temperature Materials Often Must Withstand Fluctuating Conditions With <u>Multiple</u> Reactive Species

- Conventional heat-resistant materials rely on a single-type of protective scale to manage corrosion (typically Al_2O_3, Cr_2O_3, or SiO_2)

- Many process environments have fluctuating conditions and multiple corrodants such that scales are not protective under all conditions encountered

- "Smart" scale concepts are being explored for this and other applications at high temperatures

Multiple Capabilities Are Necessary To Understand And Mitigate Corrosion And Degradation Processes

- Thermogravimetry
- Specialized facilities for controlled exposures
- Thermodynamic and kinetic modeling
- Traditional metallography
- EMPA (microprobe)
- Auger
- Raman spectroscopy
- X-ray diffraction (conventional and synchrotron)
  - structure determination
  - stress measurements
- Electron microscopy

ORNL Has Pioneered Using TEM/STEM For Analyzing Oxidation Products And Protective Coatings
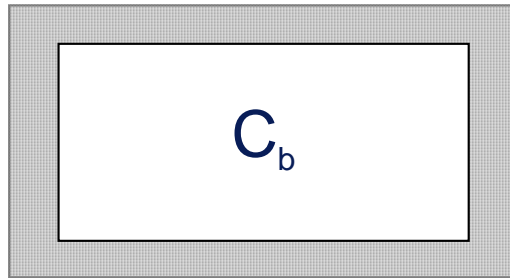

W
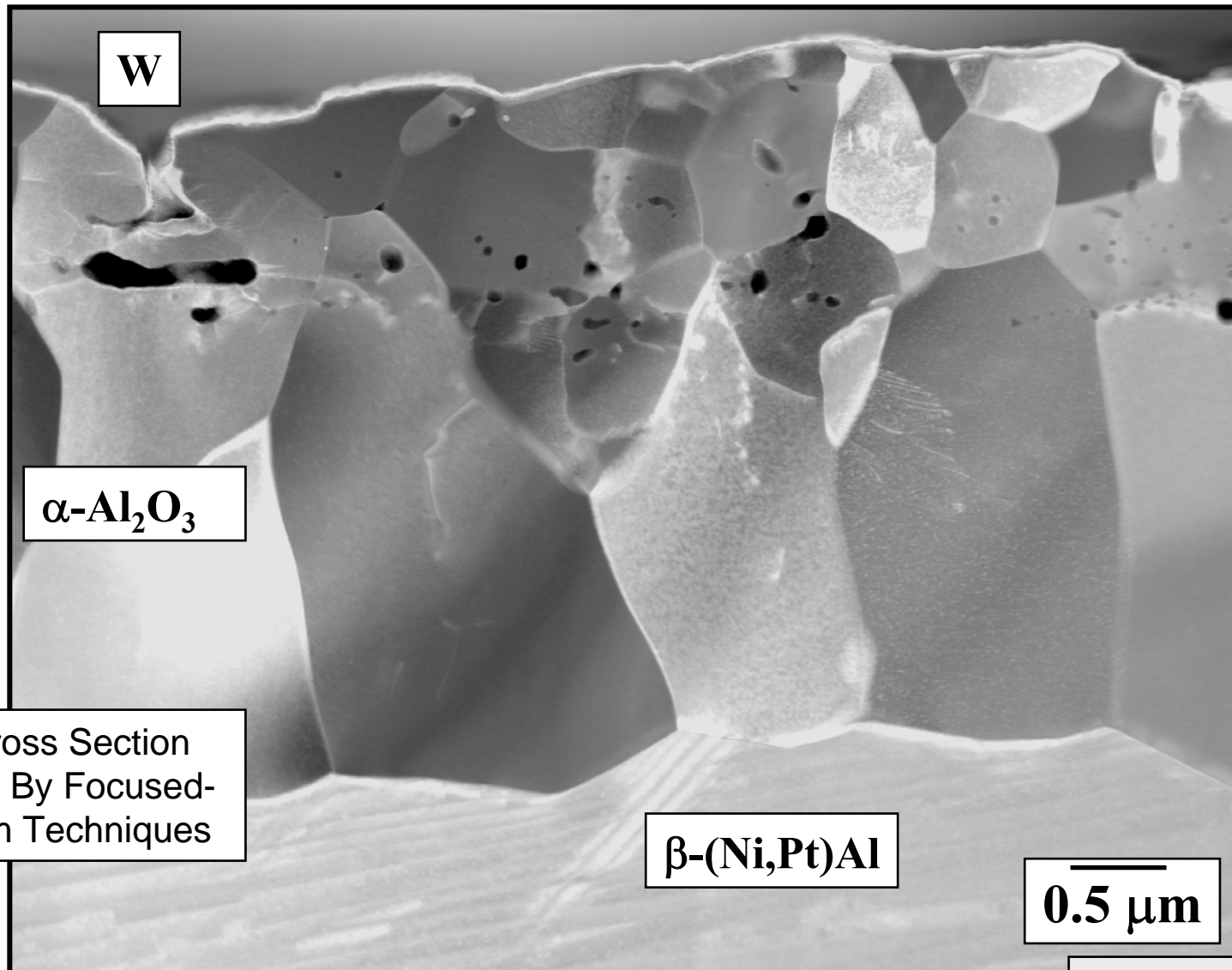
α-Al$_2$O$_3$

TEM Cross Section Prepared By Focused-Ion-Beam Techniques

β-(Ni,Pt)Al

0.5 μm
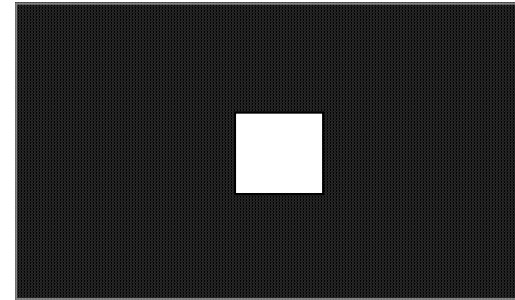
700 1-h cycles, 1150°C

More et al.

Lifetime Approaches Are Evaluated In A Number Of High-Temperature Corrosion Projects
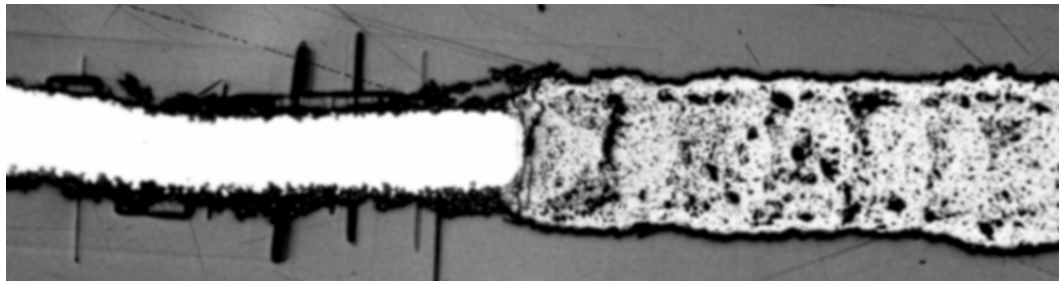
C_b

[Cr], [Al] > C_b

[Cr], [Al] < C_b

Breakaway oxidation when C_b is reached

at t_b :

Al_2O_3 Formation

Fe-based oxides

500 µm

1101 h, 1300°C

Wright, Pint, Tortorelli
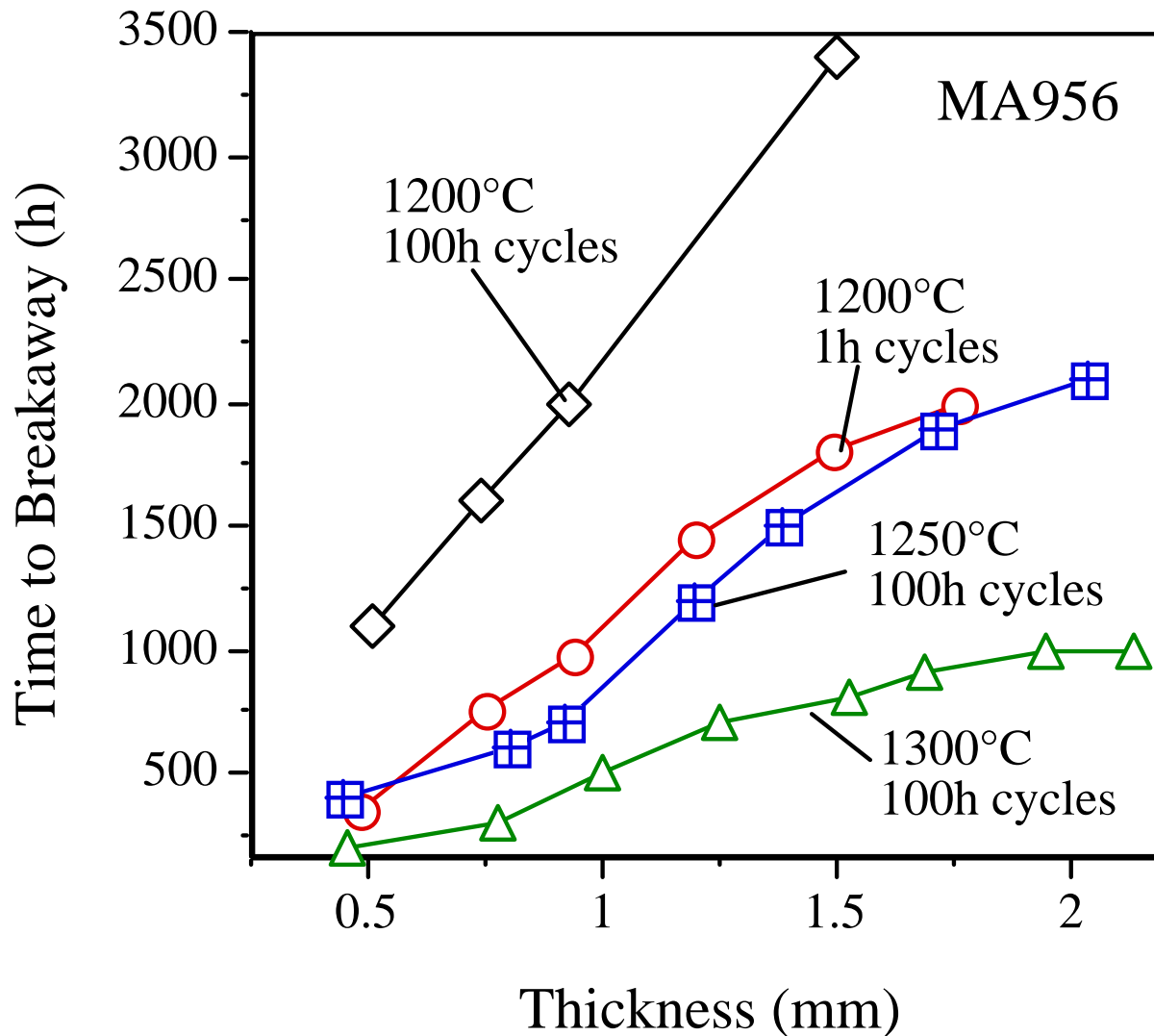
Oxidation Lifetime Modeling

For alumina formers:

$$t_b = [4.4 \times 10^{-3} \bullet (C_o - C_b) \bullet \rho \bullet d \bullet k^{-1}]^{1/n}$$

Dependent on:
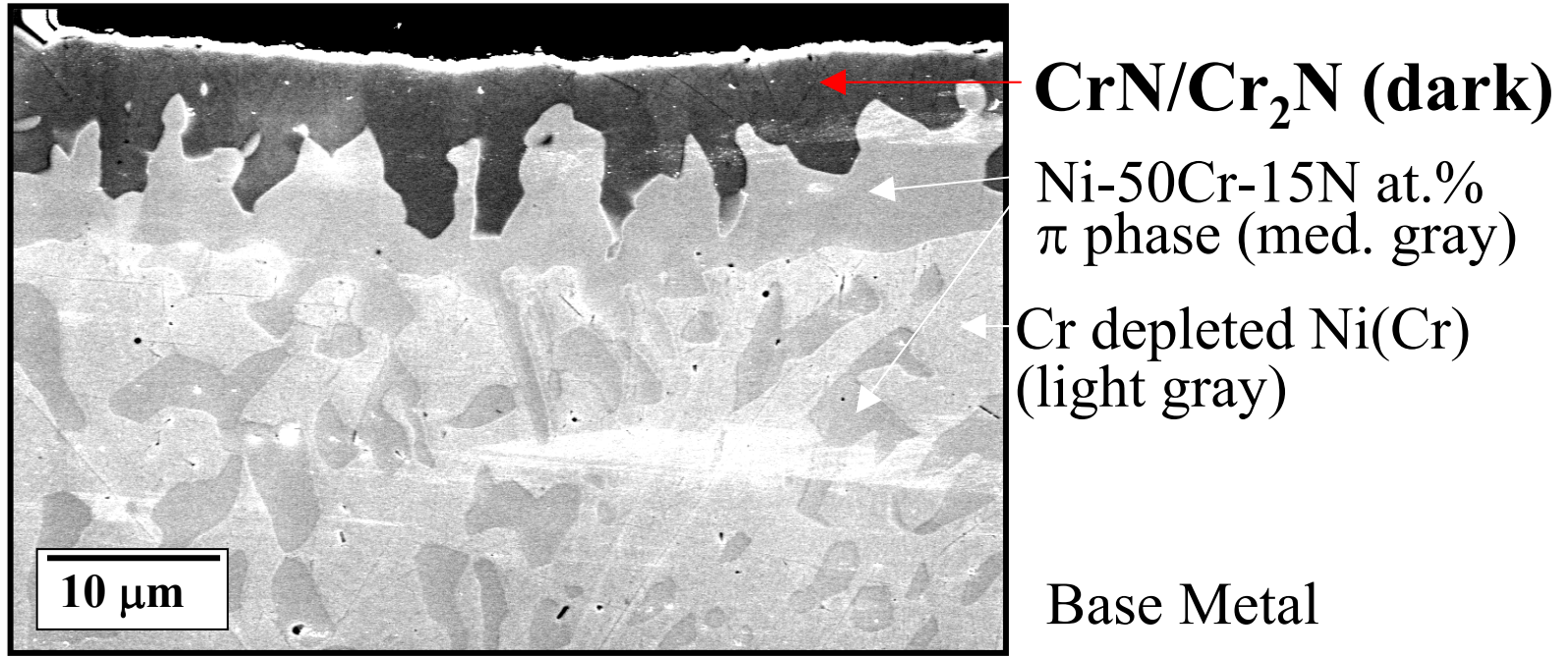- Available Al (C_o, d)
- Al Consumption (k)
- Al Diffusion In Alloy
- C_b

Approach is of particular interest for work with thin-walled components and water vapor effects

# Ultimately, Want To Predict Lifetime Under Various Oxidation Conditions

MA956

1200°C
100h cycles

1200°C
1h cycles

1250°C
100h cycles

1300°C
100h cycles

Time to Breakaway (h)

Thickness (mm)

Wright, Pint, Walker

Nitridation Is Being Studied As A Degradation Phenomena As Well As A Synthesis Tool

CrN/Cr$_2$N (dark)

Ni-50Cr-15N at.% π phase (med. gray)

Cr depleted Ni(Cr) (light gray)

Base Metal

Nitrided Model Ni-50Cr wt% Alloy
(1100°C, N$_2$, 24 h)

Adherent, inward-growing Cr-nitride favorable for use as a protective but conductive layer for PEM bipolar plate

Brady et al.

Degradation Of Refractories For Black Liquor Gasification Applications Is Being Studied
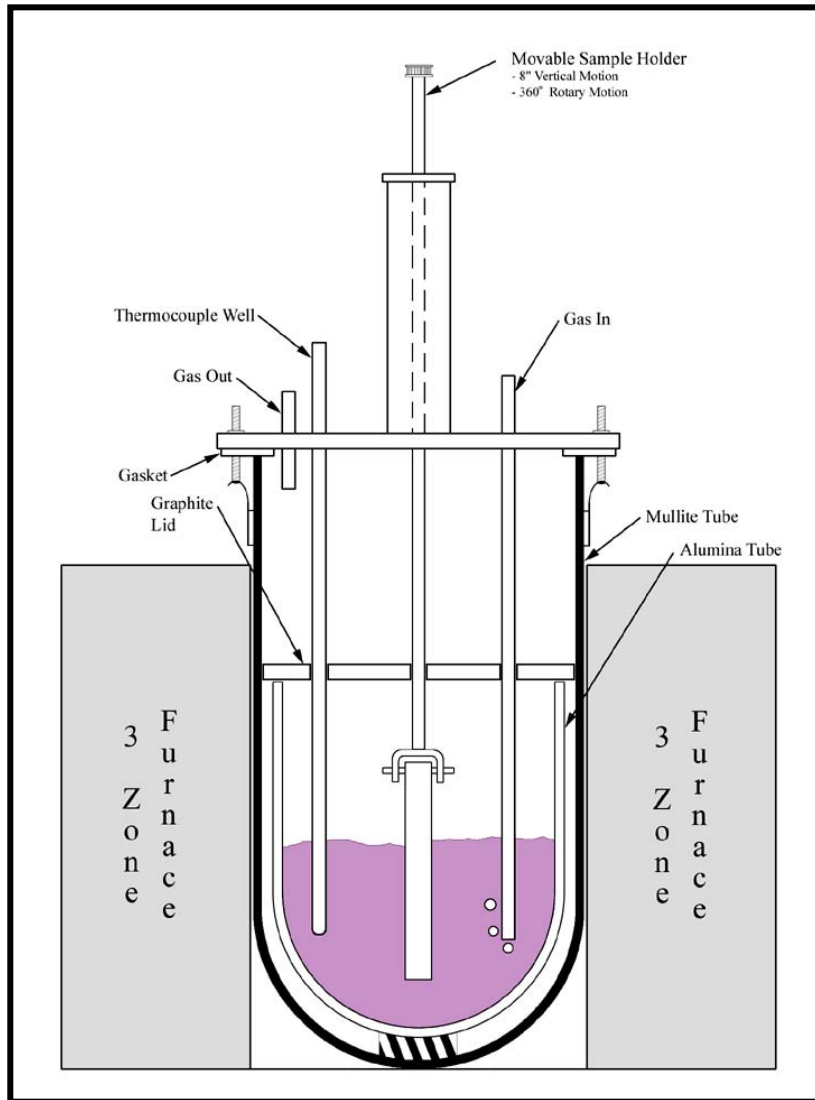
Molten smelt continuously mixed with bubbling Ar gas

- **50 - 250 h**

- **1000°C**

Keiser, Peascoe-Meisner, Hubbard

Immersion Exposures Of Commercially Available Refractories To Smelt Showed Varied Responses


Dense ʊ-Alumina (Al_2O_3)

Magnesia Alumina Spinel ($MgAl_2O_4$)

New or modified refractory compositions and surface treatments are being explored

Developmental Cr-Based Alloys Are Being Examined For Use In Molten Salt Environments

- Conventional alloys are aggressively attacked in molten smelt

- Oxide dispersion ductilized Cr alloys exhibit promising corrosion resistance (94Cr – 6MgO, wt.%)

- Targeted applications: thermowells, protective coatings

80 mm

Cr alloy rods for test exposure in gasifier
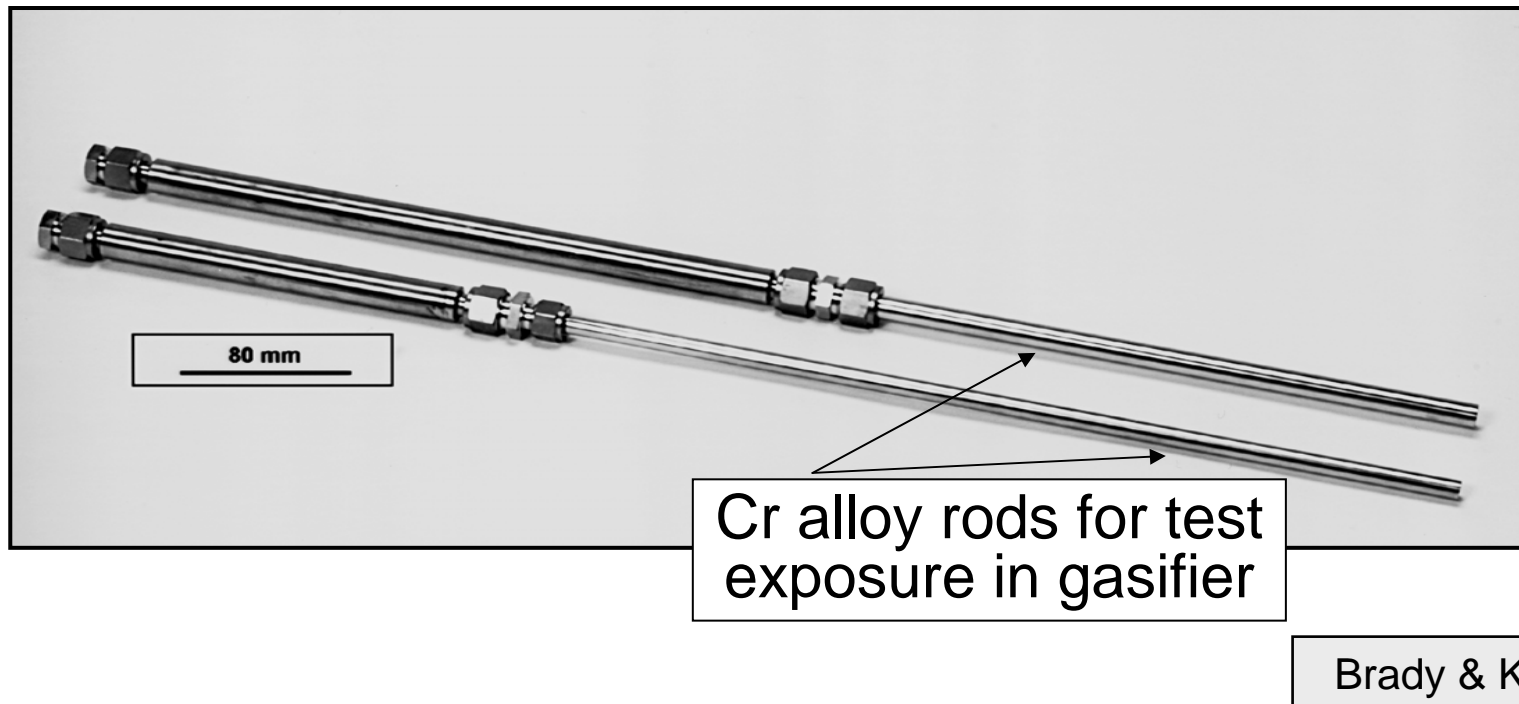
We Often Relate Our Work To "Real" Products And Environments Through Field Exposures And Analyses

- Recuperators

- Ceramic composites and coatings for combustor liners in gas turbines

- Hot-gas filters for coal-derived syngas

- Failure modes for commercial TBCs

- Floor and wall tubes from black liquor recovery boilers

- Digester corrosion in paper plants, use of electrochemical noise measurements for in-plant monitoring

- Alloys and refractories for smelt and slag applications

- Dross formation in Al melting

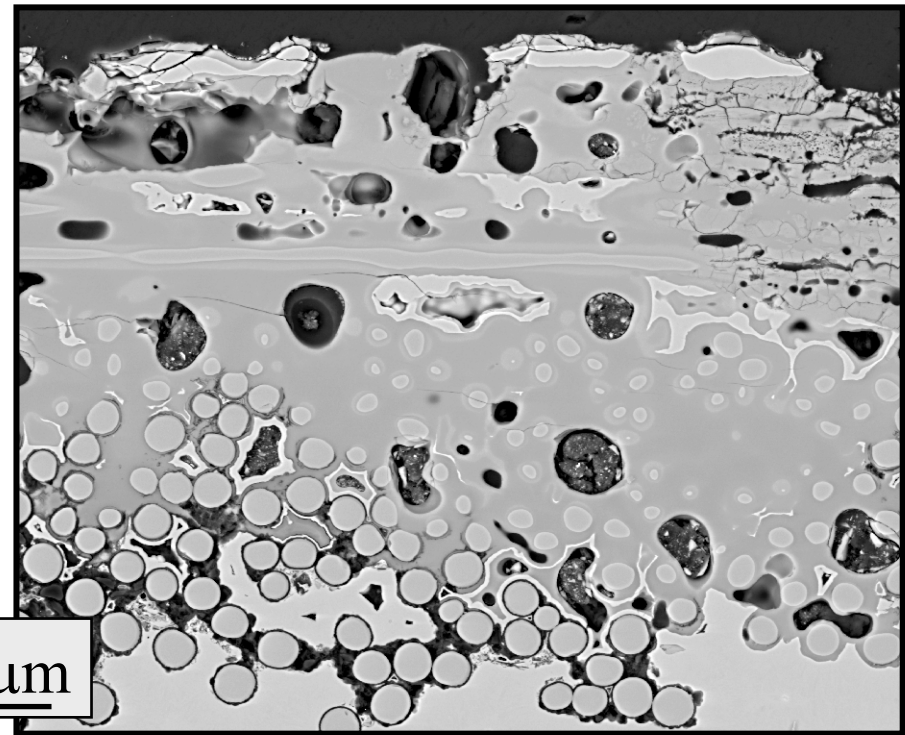# EBC/SiC/SiC Combustor Liners For Solar Turbines Centaur 50 Engine
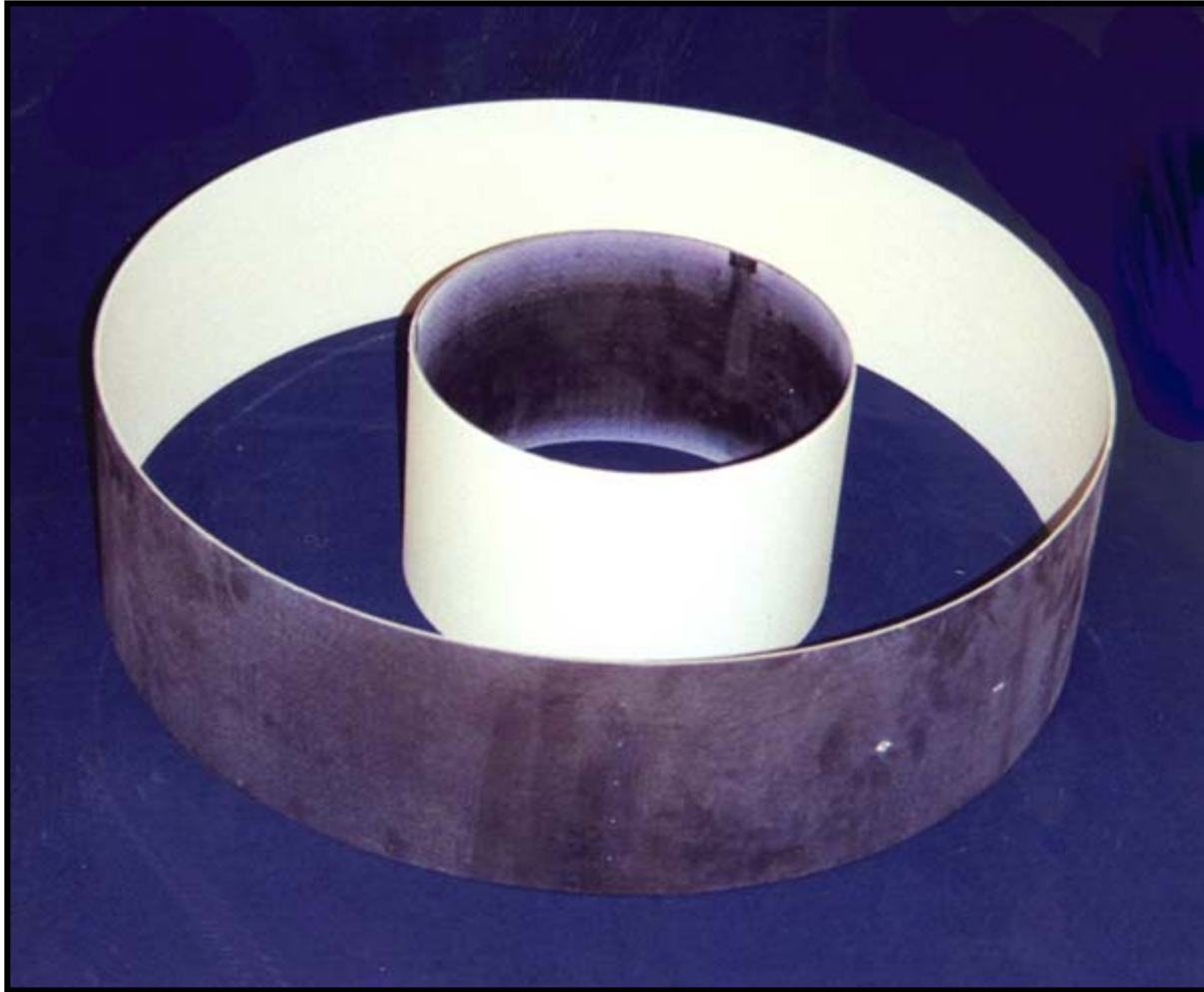
Composite Damage Observed In Lab Exposures Was Very Much Like That Of Actual Combustor Liners

Lab Exposure
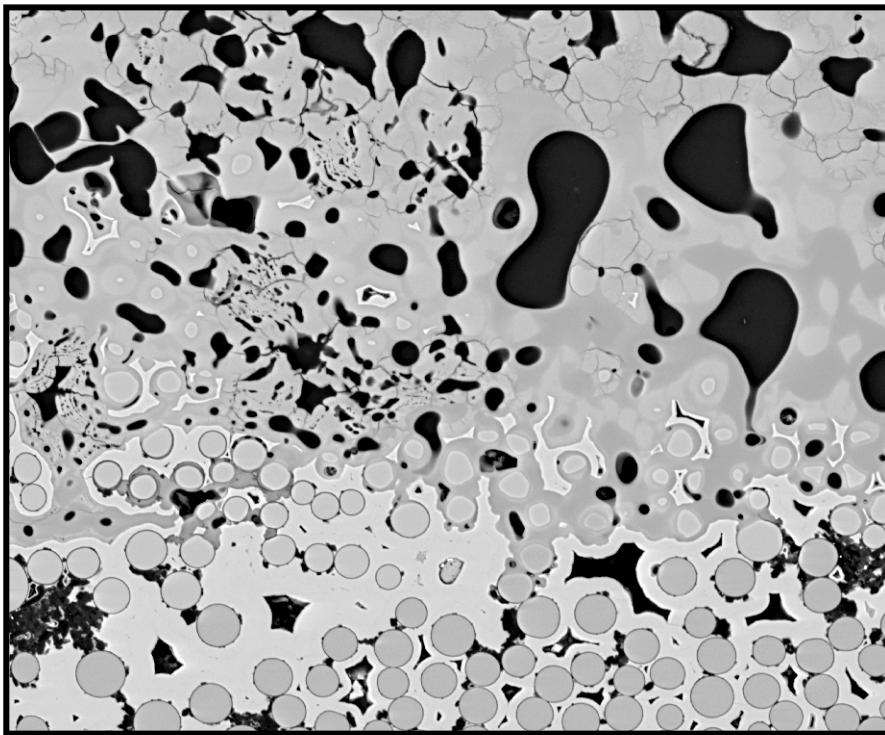
Engine Test

CVI SiC/BN/SiC, 1200°C, 1.5 atm H_2O

A Variety Of R&D Approaches Are Used To Study High-Temperature Corrosion & Environmental Effects

- Address scientific problems underlying protective scale formation as well as issues associated with materials and technology development, industrial processes, and lifetime prediction

- Design, assemble, and operate specialized (in some cases, unique) equipment for studies of materials behavior in controlled environments

- Evaluate field results and relate to laboratory studies through analyses and modeling

- Use state-of-the-art materials characterization techniques